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Modification is a perceptual phenomenon. Although the chemical mixtures that are used to change odor perception usually do not react outside of the olfactory organ, modern theory does postulate that chemical complexes involving enzymes are active within the organ. Changes in the way these complexes form may explain why mixtures of odorants vary from individual chemicals in the way they are perceived.

Odors and Their Mixtures

Odor is that property of a substance that makes it perceptible to the sense of smell. Although it is certain that odor is caused by molecular structure, there remains little predictability about this correlation of odor with structures. It is known from experience that certain chemical classes have certain types of odor (see also Flavor characterization), but even an expert cannot predict what an unfamiliar molecule or mixture will smell like.

Intensity perception. The measurable properties of odor perception are its intensity and its character. The measurement and expression of odor mixture intensity can be achieved in a number of ways, but they are almost all subjective. The simplest but the most subjective method is the use of a hedonic scale. The format possibilities are many, eg, 0 = no odor, 1 = barely perceptible, 2 = distinct, 3 = strong, 4 = very strong, and 5 = overpowering.

One of the most objective measures of an odorant's intensity is its threshold which, however, reflects the intensity of only one specific odorant concentration, ie, the weakest that can be detected.

All the senses, including smell, relate to the psychophysical law (Stevens' law) as expressed by the power equation:

$$\psi = k\phi^{\beta}$$

where ψ is the perceived intensity of the sensation, ie, the odor; k is a constant; and ϕ is the physical intensity of the stimulus, ie, the odorant. Generally, the sensation varies as a power function of the stimulus. In olfaction, the power β is less than one.

Character perception. Odor character is purely subjective. Several chemicals have been experimentally characterized by scaling the degrees to which each chemical possesses subjective reference qualities, eg, burnt, fruity, and spicy. But no method exists that can reliably characterize odors.

Mixture perception (modification). Many odorous and nonodorous chemicals are used to control odors, but only those that work essentially by altering the way the nose perceives the character and intensity are true odor modifiers.

Products

Although the original intent of deodorizers was to reduce malodor, use for decorative purposes is becoming an important factor. The active ingredient of masks and counteractants are oils: essential oils, which are fragrance extracts from flowers, herbs, fruits, and trees; animal extractives; and aroma chemicals, which may be either natural or synthetic.

ROBERT H. BUCKENMAYER
Airwick Industries, Inc.

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OIL SANDS. See Tar sands.

OILS, ESSENTIAL

A simple, though incomplete, definition of essential oils is the following: an essential oil is the predominantly volatile material isolated by some physical process from an odorous single-species botanical. Over 3000 oils have been identified from the vast number of plant species and several hundred have been commercialized. Of these, some are extremely rare and produced in only kilogram quantities, eg, violet oil, concretes (flower extracts), and angelica root oil.

Essential oils are now generally manufactured close to the growing area. Product quality has suffered, however. Essential oils are easily adulterated and this technology has not been overlooked by isolated local producers.

Essential oils are isolated from various plant parts, such as leaves (patchouli), fruit (mandarin), bark (cinnamon), root (ginger), grass (citronella), wood (anyris), heartwood (cedar), gum (myrrh), balsam (tolu balsam), berries (pimenta), seed (caraway), flowers (rose), twigs (clove stems), and buds (cloves). These plant parts are processed to yield their quintessences or essential oils, which are mostly devoid of cellulose, glycerides, starches, sugars, tannins, salts, and minerals which also occur in these botanicals.

The common physical method for isolating essential oils from the botanical is steam distillation, wherein small amounts of nonvolatiles may be carried over. Some oils are expressed. Many flower oils are extracted with a purified petroleum solvent.

Essential oils are generally liquid at room temperature; however, some are semisolid, such as *Mentha arvensis* (Brazilian mint), and several are solid, eg, oil of guaiac wood.

The cultivation of essential oil-bearing plants has kept pace with modern agricultural methods. Hybrids are grown to yield oils of specific odor, flavor, or properties.

Essential oils are used as such for flavors and fragrances, but products derived from, or based on essential oils have large volume usage for specific applications. Essential oils are concentrated, rectified, extracted, or chemically treated to further isolate vital components, purify, adjust properties, or increase the concentration of significant flavor or fragrance components (see Flavors and spices; Perfumes).

Composition

The volatile components of essential oils usually contain fifteen carbon atoms or less. However, seed oils contain long-chain fatty acids or esters and even glycerides that are carried over in distillation; the amounts of these components are very low.

Essential oils basically are made up of carbon, hydrogen, and oxygen, and occasionally nitrogen and sulfur. The largest class of components is the terpenes which have ten carbon atoms and are head-to-tail condensation products of two isoprene molecules (see Terpenoids). The terpenes may be aliphatic, alicyclic, or bi- and tricyclic of varying degrees of unsaturation up to three double bonds.

It is not uncommon for an essential oil to contain over two hundred components and often the trace substances (in ppm) are essential to the odor and flavor. The absence of even one component may change the aroma. The same species of botanical, grown in different parts of the world, usually has the same components; however, climatic and topographical conditions affect plants and can alter the essential oil quantitatively, but rarely qualitatively.

Production

In the botanical, the essential oil is present in oil sacs. It is isolated by comminution, and the action of heat, water, and solvents.

Steam distillation. Steam or hydrodistillation is the preferred method for producing essential oils, employing either water, wet steam, or steam.

Extraction. An essential oil that is sensitive to heat, eg, jasmine or tuberose, or contains an essential nonvolatile constituent, eg, piperine in black pepper, is extracted with a solvent (see Extraction).

Synthetic Substitutes for Essential Oils

Fluctuations in the cost and availability of natural oils and the high cost of some oils have induced users to seek substitutes. Several former large-volume oils have been replaced by synthetics because of large volume demands. The expensive variations in cost are especially evident in essences such as rose, jasmine, violet, lilac, neroli, etc. Duplication of these items is economically worthwhile. Modern techniques and instru-

mentation offer the possibility for total analysis of these oils. This route has been undertaken by the primary fragrance and flavor companies throughout the world in the attempt to find economic and available substitutes. Nonetheless, there is a trend away from synthetic oils because complete duplications are in most cases not technically, aesthetically, or economically possible.

Health and Safety Factors

Most essential oils, since they are natural and have a history of use, are considered GRAS (generally recognized as safe) by the FDA. Safety and toxicity testing and evaluations and regulations are different for food additives than for fragrance oils and cosmetics (qv). Some oils can be used for both purposes, including celery, rose, and black pepper. Some oils, such as cinnamon oil, can be used in flavors, but not in fragrances because of skin irritation.

Commercial Essential Oils

The commercial essential oils include allspice (pimenta berry), bitter almond, amyris, anise, star anise, sweet basil, bay (myrcia), bergamot, sweet birch, bois de rose (rosewood), camphor, cananga, caraway, cardamom, cassia, cedarwood, cinnamon, citronella, clove, coriander, eucalyptus, geranium, ginger, grapefruit, jasmine, juniper, labdanum, lavandin, lavender, lemon, distilled lime, japanese mint, neroli, nutmeg, ocotea, bitter orange, sweet orange, origanum, orris root, palmarosa, patchouli, black pepper, peppermint, petitgrain bigarade, pine, pinus pumilio, rose, rosemary, dalmatian sage, sage clary (sage muscatel), East Indian sandalwood (santal), spearmint, spike lavender (spike), thuja (cedarleaf), thyme, turpentine, vetiver, wintergreen, and ylang ylang.

JAMES A. ROGERS, JR.
Fritzsche, Dodge & Olcott, Inc.

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OIL SHALE

Oil shale consists of a marlstone-type sedimentary inorganic material hat contains complex organic polymers that are high molecular weight olids. The organic kerogen is a three-dimensional polymer, insoluble in onventional organic solvents, and associated with small amounts of a enzene-soluble organic material, bitumen. Oil-shale deposits were formed n ancient lakes and seas by the slow deposition of organic and inorganic emains from the bodies of water. As the waters stagnated and dried, the eposits compacted. The geology and the composition of inorganic and rganic components of oil shale varies with deposit location.

eserves

Oil-shale deposits occur widely throughout the world; estimates of the esources by continent are given in Table 1. Characteristics of many of he world's best-known oil shales are summarized in Table 2. Oil-shale eposits in the United States occur over a wide area. The most extensive eposits, which cover ca 647,000 km^2 (250,000 mi^2), are the Devonian-Mississippian shales of the eastern United States. The richest U.S. oil hales are in the Green River formation of Colorado, Utah, and Wyoming.

etorting

Thermal decomposition of oil shale. The thermal decomposition of l shale, ie, pyrolysis or retorting, yields liquid, gaseous, and solid roducts. The liquid, which is produced by pyrolysis, is in the form of a apor or mist. The remaining organic carbon remains on the retorted hale, the mineral matter, as a cokelike deposit. The amounts of oil, gas,

Table 1. Shale-Oil Resources of the Populous Land Areas, 10^9 m^3[a]

Shale-oil yield range, L/t[c]	Total resource[b]			Known resources: marginal or submarginal recovery			Recoverable known resources
	21–42	42–104	104–417	21–42	42–104	104–417	42–417
Africa	71,500	12,700	636	small	small	14	1.6
Asia	93,800	17,500	874	na	2	11	3.2
Australia and New Zealand	15,900	3,200	159	na	small	small	small
Europe	22,260	4,100	223	na	1	6	4.8
North America	41,400	8,000	477	350	254	99	13
South America	33,400	6,400	318	na	119	small	8
Total	*278,260*	*51,900*	*2,687*	*350*	*376*	*130*	*30.6*

[a]To convert m^3 to bbl, divide by 0.159.
[b]Includes oil shale in known resources, in extensions of known resources, and in undiscovered but anticipated resources.
[c]To convert L/t to gal/short ton, multiply by 0.2397.

Table 2. Properties of Oil Shales

	Australia (Glen Davis)[a]	Brazil (Trembe-Taubate)[a]	Canada (Nova Scotia)[b]	Manchuria (Fushun)[b]	New Zealand (Orepuki)[b]	South Africa (Ermelo)[a]	Spain (Puertolleno)[a]	United States (Colorado)[a]
Modified Fischer assay								
oil, L/t[c]	414	156	257	38	331	228	234	122
oil, wt%	30.0	11.5	18.8	3.0	24.8	17.6	17.6	9.3
water, wt%	0.7	6.2	0.8	4.9	8.3	3.0	1.8	1.0
spent shale, wt%	64.1	78.4	77.7	90.3	57.6	75.6	78.4	87.5
gas and loss, wt%	4.3	3.9	2.7	1.8	9.3	3.8	2.2	1.6
conversion of organic material to oil,[d] wt%	66	59	60[e]	33	45	34	57[e]	70
Rock characteristics								
sp gr (at 16°C)	1.60	1.70		2.29	1.46	1.58	1.80	2.23
heating value, MJ/kg[f]	18.8	8.2	12.6	3.4	21.3	19.1	12.5	5.1
ash, wt%	51.6	71.4	62.4	82.7	32.7	42.5	62.8	66.9
organic carbon, wt%	39.8	16.5	26.3	7.9	45.7	43.8	26.0	11.3
Assay oil								
sp gr (at 16°C)	0.89	0.88	0.88	0.92	0.90	0.93	0.90	0.91
carbon, wt%	85.4	84.3		85.7	83.4	84.8		84.6
hydrogen, wt%	12.0	12.0		10.7	11.8	11.1		11.6
nitrogen, wt%	0.5	1.1			0.6		0.9	1.8
sulfur, wt%	0.4	0.2			0.6	0.6	0.3	0.5
Ash analysis, wt%								
SiO_2	81.5	55.8	61.1	62.3	44.2	61.3	56.6	43.6
Al_2O_3	10.1	26.7	30.1	26.7	28.1	30.5	27.6	11.1
Fe_2O	3.0	8.5	5.0	6.1	20.5	2.9	9.1	4.6
CaO	0.8	2.8	1.1	0.1	4.6	1.6	2.6	22.7
MgO	0.8	3.7	1.6	1.8	1.4	1.7	2.2	10.0
other oxides	3.8	2.5	1.1	3.0	1.2	2.1	1.9	8.0

[a]Average sample.
[b]Selected sample.
[c]To convert L/t to gal/short ton, multiply by 0.2397.
[d]Based on recovery of carbon in oil from organic carbon in shale.
[e]Carbon content of oil ca 84 wt%.
[f]To convert MJ/kg to Btu/lb, multiply by 430.4.

and coke which ultimately are formed depend on the heating rate of the oil shale and the temperature–time history of the liberated oil.

Numerous kinetic mechanisms have been proposed for oil-shale pyrolysis reactions. The kinetics appear to be adequately represented by first-order rate mechanisms, eg,

$$\text{kerogen} \xrightarrow{k_1} \text{bitumen} + \text{gas} + \text{coke}$$

$$\text{bitumen} \xrightarrow{k_2} \text{oil} + \text{gas} + \text{coke}$$

Most oil-shale retorting processes are carried out at ca 480°C to maximize liquid-product yield.

Aboveground retorting. The first aboveground oil-shale processes were batch or semibatch, and modern commercial contenders are continuous in both feed and product removal. Room-and-pillar mining is used for commercial aboveground retorts. Open-pit mining has the potential for greater resource recovery but requires off-site spent-shale disposal.

The heat required for retorting is transferred to the oil shale in four main types of retorts. In Type-1 retorts, the heat must be transferred through the vessel wall to the oil shale. A combustion zone within the